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New Binary Lanthanide Catalysts for Stereospecific Diene Polymerization

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ABSTRACT: New binary lanthanide catalysts composed of tetrahydrofuran adducts of lanthanide chlorides and triethylaluminum in hydrocarbon solvents which stereospecifically polymerize butadiene and isoprene are described. For example, the catalyst composed of $NdCl_3{\cdot}2THF$ with Et_3Al can be used to form both polybutadiene and polyisoprene with 97% and 95% cis-1,4 units, respectively, with good activity. The organometallic intermediates in these polymerizations have been shown to be reactive enough to be successfully quenched with carbon dioxide to form carboxylic acids.

The discovery of lanthanide and actinide catalysts for stereospecific polymerization of dienes has led to the development of Ziegler–Natta catalysts from f-orbital elements and confirmed the belief that the expansive coordination as well as the f-symmetry valence orbitals of the lanthanides and actinides can display useful catalytic properties related to those of d-transition metals. In stereospecific polymerization of dienes with Ziegler–Natta type catalysts, only lanthanide catalysts and uranium catalysts are known to give high *cis*-1,4-polybutadiene, high *cis*-1,4-polyisoprene, and their copolymer containing both monomer units with high cis-1,4 geometry.[4,5] Consequently, further research into and development of lanthanide catalysts for diene polymerization has aroused great interest.

Shen, Ouyang, et al.[6] first used a lanthanide catalyst which was a binary system composed of $LnCl_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Er, and Yb) and AlR_3 (R = Et, *i*-Bu) in polymerization of butadiene. The resulting catalysts' stereospecificity was high, but their catalytic activity was rather low. Throckmorton modified the catalyst system from binary to a ternary system (cerium octanoate–AlR_3–halide) and found polymerization activity was increased.[7] However, a drawback of this system is the requirement that the Ce-containing residues must be completely removed from the resulting polymers because cerium ion can promote rubber oxidation. Since 1970, Chinese chemists have developed a new "family" of lanthanide catalysts based on neodymium compounds or a mixture of neodymium and praseodymium compounds. These elements were found to be the most active elements in the series of lanthanides. Some three-component systems which were first developed include lanthanide naphthenate, lanthanide carboxylates, or lanthanide phosphates together with AlR_3 and added halide.[8] These catalysts are used for butadiene polymerization, for isoprene polymerization, and for butadiene and isoprene copolymerization. Subsequently, it was found that the addition of suitable amounts of alcohol to the original system ($LnCl_3$–AlR_3) led to greatly enhanced activities without any decrease in stereospecificity.[9] Further investigation revealed that the lanthanide halide first reacts with the added alcohol to form an alcoholate which then reacts with AlR_3 to form an active catalyst. Thus, a new efficient binary system of $LnCl_3{\cdot}3ROH$–AlR_3 has been established. Other binary catalysts such as $NdCl_3{\cdot}3P_{350}$ (P_{350} = $((CH_3(CH_2)_5CH(CH_3)O)_2POCH_3)$)[8] or $NdCl_3{\cdot}3TBP$ (TBP = triisobutyl phosphate)[10] with AlR_3 were also developed. Recently, a few USSR patents concerning polymerization of dienes using $LnCl_3{\cdot}Me_2SO$ (Me_2SO = dimethyl sulfoxide) or $LnCl_3{\cdot}n$HMPA (HMPA = hexamethylphosphoramide) with AlR_3 have been cited.[11]

Here we report that a new binary system composed of $NdCl_3{\cdot}2THF$ with $AlEt_3$ also is an efficient catalyst for diene polymerization in hydrocarbon solvents. Since THF is a very useful solvent for many organometallic syntheses and since it does not react with AlR_3 other than to form a Lewis acid–base complex, this catalyst system will be an attractive system for study of these lanthanide polymerization catalysts, their reactions, and possible intermediates in the polymerization process.[12] In addition, we have shown the reactive nature of the organometallic intermediates in these polymerizations by trapping polymeric intermediates with carbon dioxide.[13]

Results and Discussion

THF is a very useful solvent for many organometallic syntheses in part because of its aprotic nature and its ability to complex with metal salts. It was known that anhydrous lanthanide chloride salts also readily form

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Table I
^{13}C NMR Data for 1,4-Polyisoprene

polymer	carbon position[a,b] α	β	γ	ζ	ε
natural cis-1,4	134.8	124.6	31.8	26.3	22.9
synthetic cis-1,4	134.9	124.8	31.8	26.1	22.7
Ln cis-1,4[c]	134.9	124.8	31.9	26.2	23.0
natural trans-1,4	134.5	124.9	39.3	26.4	15.3

[a] Chemical shifts are given relative to benzene (δ 128.5). Data for natural and synthetic polyisoprene are from ref 17. [b] Positional labeling for carbon according to ref 17. [c] Chemical shifts measured for lanthanide catalyst derived *cis*-1,4-polyisoprene were measured relative to benzene-d_6 (δ 128.0).

complexes with THF and that these complex salts can be isolated in the form of THF adducts, $LnCl_3{\cdot}nTHF$. In the case of Nd and Pr, $n = 2$.[14] We have found that when these THF complexes are treated with an appropriate amount of $AlEt_3$ in hydrocarbon solvents, efficient catalysts for stereospecific polymerization of butadiene and isoprene are formed.

Figures 1 and 2 show typical IR spectra of the polybutadiene and polyisoprene obtained with the $NdCl_3{\cdot}2THF$ catalyst. The peak intensities at 738, 911, and 967 cm^{-1} in Figure 1, which are characteristic of *cis*-1,4-, 1,2-, and *trans*-1,4-polybutadiene units, respectively,[15] clearly show that the polymer obtained with this binary lanthanide catalyst has a high cis-1,4 structure. Quantitative calculations showed a cis-1,4 content of 97.1%, a 1,2 content of 0.8%, and a trans-1,4 content of 2.1%. Figure 2 shows the IR spectrum of a typical polyisoprene sample prepared with this catalyst. Absorption bands at 840 and 890 cm^{-1} are characteristic of 1,4 (total) and 3,4 units, respectively, while bands at 1130 and 1375 cm^{-1} are characteristic of cis-1,4 units in polyisoprene.[16] The absence of characteristic IR bands at 910 cm^{-1} (for 1,2 units) as well as the absence of bands at 1150 and 1385 cm^{-1} (for trans-1,4 units) indicated that the content of 1,2 and trans-1,4 units in the polyisoprene was negligibly small. ^{13}C NMR of the polymer confirmed the absence of trans-1,4 units in the polyisoprene (Table I). No peaks were seen at chemical shifts reported for *trans*-1,4-polyisoprene while the observed chemical shifts correlated well with those reported for *cis*-1,4-polyisoprene. Therefore, the absorption band at 840 cm^{-1} in the IR spectra can be used for the determination of the cis-1,4 content in lanthanide-derived polyisoprene. Calculations based on the intensity of this band and the intensity of the 890-cm^{-1} band indicated that this polymer had a 95% cis-1,4 content and a 5% 3,4 content. These binary catalysts thus form both polybutadiene and polyisoprene with high stereospecificity favoring cis-1,4 units in the final polymer.

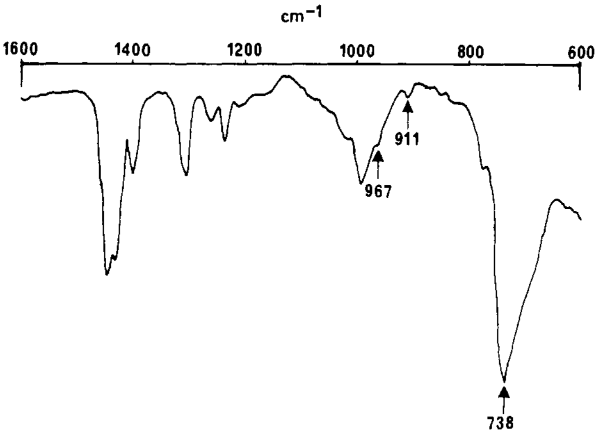

Figure 1. IR spectrum in the region 1600–600 cm^{-1} for polybutadiene prepared with $NdCl_3{\cdot}2THF–Et_3Al$ catalyst.

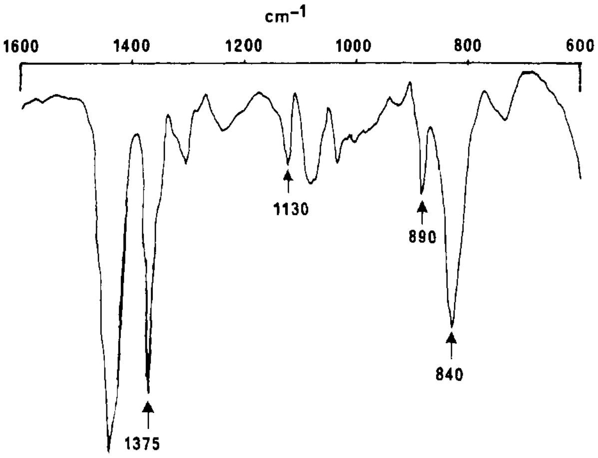

Figure 2. IR spectrum in the region 1600–600 cm^{-1} for polyisoprene prepared with $NdCl_3{\cdot}2THF–Et_3Al$ catalyst.

The activity of the present catalyst is satisfactory and is readily modified by varying the experimental conditions. Table II shows the results of butadiene polymerizations carried out with the $NdCl_3{\cdot}2THF$ catalyst at constant monomer concentration, polymerization temperature, and reaction time. Not unexpectedly, the components and amount of catalyst relative to substrate markedly affect the polymerization process. For example, when the $NdCl_3{\cdot}2THF$/monomer (mole/gram) ratio was fixed, increases in the ratio of $AlEt_3/NdCl{\cdot}2THF$ (mole ratio) led to an increase in the conversion percent and a reduction of the intrinsic viscosity of the resulting polymer. When the $AlEt_3/NdCl_3{\cdot}2THF$ (mole ratio) ratio was fixed, an

Table II
Polymerization of Butadiene with $NdCl_3{\cdot}2THF\text{-}AlEt_3$[a]

$NdCl_3{\cdot}2THF$/ butadiene, mol/g × 10^6	$AlEt_3$/ $NdCl_3{\cdot}2THF$, mol/mol	conversion, %	[η], dL/g	microstructure, % cis-1,4	1,2	trans-1,4
3	5	25.5		97.7	0.5	1.8
3	10	35.5	11.3	97.7	0.6	1.7
3	20	83.5	9.7	97.8	0.8	1.4
3	30	90.0	9.3	97.7	0.6	1.7
3	40	95.0	8.2	97.1	0.8	2.1
2	20	65.0	9.1	98.2	0.4	1.4
4	20	88.0	8.2	98.2	0.5	1.3
6	20	100.0	7.7	97.4	0.6	2.0
8	20	100.0	6.1	97.9	0.5	1.6
10	20	100.0	5.7	97.1	0.6	2.3

[a] Polymerizations were carried out at 50 °C for 5 h in heptane with an initial butadiene concentration of 10% (w/v).

Table III
Polymerization of Isoprene with $NdCl_3$·2THF-$AlEt_3$[a]

$NdCl_3$·2THF/ isoprene, mol/g × 10^6	$AlEt_3$/ $NdCl_3$·2THF, mol/mol	conversion, %	[η], dL/g	microstructure, %	
				cis-1,4	3,4
3	5				
3	10	49.0	4.6	96.0	4.0
3	20	80.0	4.4	95.2	4.8
3	30	88.0	3.8	95.9	4.1
3	40	92.0	3.4	95.4	4.6
2	20	63.5	4.6	95.2	4.8
4	20	79.0	4.4	95.1	4.9
6	20	87.5	3.9	95.1	4.9
8	20	92.0	3.5	94.8	5.2
10	20	94.0	3.4	95.0	5.0

[a] Polymerizations were carried out at 50 °C for 5 h in heptane with the monomer concentration initially at 10% (w/v).

Table IV
Diene Polymerization Using Various Lanthanide Elements in the $LnCl_3$·2THF-$AlEt_3$ System[a]

Ln	Ln/ monomer, mol/g × 10^6	$AlEt_3$/ Ln, mol/mol	butadiene			isoprene		
			conversion, %	[η], dL/g	cis-1,4	conversion, %	[η], dL/g	cis-1,4
Nd	3	20	85.0	8.7				
	5	20	98.0	7.9	97.7	88.5	4.3	95.3
Pr	3	20	69.5	8.9				
	5	20	90.0	8.0	97.9	84.5	4.6	94.5
Gd	3	20	54.0	9.0				
	5	20	65.5	8.4	97.2	51.5	4.4	96.5

[a] Polymerizations were carried out at 50 °C for 5 h in heptane with an initial monomer concentration of 10% (w/v).

Table V
Diene Polymerization with $NdCl_3$·2THF-$AlEt_3$ in Various Hydrocarbon Solvents[a]

solvent	Nd/ monomer, mol/g × 10^6	Nd/ $AlEt_3$, mol/ mol	butadiene			isoprene		
			conversion, %	[η], dL/g	cis-1,4	conversion, %	[η], dL/g	cis-1,4
heptane	3	20	83.5	9.7				
	5	20	98.0	8.0	97.9	89.0	4.7	94.9
cyclohexane	3	20	76.0	9.1				
	5	20	88.0	8.8	98.1	75.0	3.3	95.3
toluene	3	20	77.0	7.3				
	5	20	85.0	6.8	97.6	69.5	3.5	95.9

[a] Polymerizations were carried out at 50 °C for 5 h with an initial monomer concentration of 10% (w/v).

increase in the $NdCl_3$·2THF/monomer (mole/gram) ratio led to an increase in the conversion percent and a reduction of the polymer's intrinsic viscosity. However, the microstructure of the polymers obtained was not changed under these varying conditions. These polymers always had a high cis-1,4 content (as high as 97%). Generally, a catalyst level of 10^{-6} mol/g (Nd/monomer) and an $AlEt_3$/$NdCl_3$·2THF ratio of 20–30 mol/mol suffice to form polybutadiene with >80% conversion with an intrinsic viscosity of 7–9 dL/g and with ca. 97% cis-1,4 units (all polymerizations were carried out on a small scale using only 2 g of monomer). In the case of polyisoprene, similar effects were observed (cf. Table III). The catalyst activity for isoprene polymerization seemed to be less than that for butadiene polymerization. The intrinsic viscosity of the polyisoprene polymers was 3–5 dL/g under typical conditions. The cis-1,4 content of the polyisoprene also did not vary with polymerization reaction conditions. All of the polyisoprene polymers had ca. 95% cis-1,4 units.

In addition to neodymium, most of the other lanthanide halides also form active catalysts when the corresponding THF complexes are allowed to react with Et_3Al in hydrocarbon solvents. Table IV gives representative polymerization data for catalysts derived from praseodymium and gadolinium halides. While these other lanthanides are effective catalysts, their activities were less than that of neodymium. The reactivity order Nd > Pr > Gd[4a] parallels that of other lanthanide diene polymerization catalyst systems. The microstructure of the diene polymers, however, did not change with changes in lanthanide halide used to prepare the polymerization catalyst.

The $NdCl_3$·2THF–Et_3Al catalyst works both in heptane and in other hydrocarbon solvents such as cyclohexane and toluene (Table V). This catalyst was ineffective in pure THF. Although the activities of the $NdCl_3$·2THF–Et_3Al catalyst were diminished in toluene and cyclohexane as well, the diene polymerization catalyst was reasonably active in these solvents and the polymerization solutions were more homogeneous in appearance than their heptane counterparts because of the higher solubility of the diene polymers in these solvents. The cis-1,4 content was unaffected by these solvent changes.

Previously it has been suggested that the polymerization of dienes with lanthanide catalysts under certain conditions, e.g., lower Al/Ln molar ratios, proceeds by a "living polymer" mechanism. Evidence for this claim includes successful block copolymerizations.[4a] This suggests that lanthanide catalysts should also be useful for preparing polymers with functional end groups (e.g., CO_2H and OH) by reaction of the reactive polymeric intermediates with suitable reactants. We have found that this is indeed the case. When a butadiene polymerization carried out in cyclohexane was quenched with CO_2, a polymer with carboxylate groups was obtained as judged by observation of a carboxylate stretch at 1560 cm^{-1} in the IR spectrum. Protonation of this polymeric carboxylic with either HCl or *p*-toluenesulfonic acid led to a carboxylic acid polymer (1725-cm^{-1} absorption in the IR spectrum).

Experimental Section

General Procedures. Commerical butadiene was purchased from Matheson Co. and was purified by passing it through three successive columns which contained drying agent ($CaSO_4$), KOH, and molecular sieves, respectively. Isoprene (>99.0%, Aldrich Chemical Co.) was freed of inhibitor by distillation, refluxed with Na for 4 h, distilled with an oil bath preheated to 60–80 °C, and stored over molecular sieves prior to use. Heptane, cyclohexane, or toluene used as polymerization solvents was purified by refluxing with Na or molecular sieves and then distilling under nitrogen and storing over molecular sieves. $AlEt_3$ was a commercial product obtained from Research Organic/Inorganic Chemical Co. Anhydrous lanthanum halides ($NdCl_3$, $PrCl_3$, $GdCl_3$) were prepared by sublimating a mixture of the corresponding hydrate and NH_4Cl at 200–350 °C under vacuum according to the method of Taylor et al.[18] Carbon dioxide was purchased from Matheson Co. and was dried by passing it through a 10-cm 8-mesh anhydrous $CaSO_4$ column. THF complexes of lanthanum halides were prepared by extracting the anhydrous halides with THF[14] in the general procedure described below for $NdCl_3 \cdot 2THF$. Anhydrous $NdCl_3$ (3.6 g) was placed in the thimble of a Soxhlet extraction apparatus in a drybox and extracted with 100 mL of boiling THF that had previously been distilled form blue sodium–benzophenone. After ca 10 h of extraction was finished, the pot flask contained a solution of $NdCl_3$ tetrahydrofuranate together with a precipitate. After cooling, the precipitates were filtrated, washed with THF, and dried under vacuum at room temperature to obtain 4.8 g of product. The yield was 85% (according to $NdCl_3 \cdot 2THF$). Anal. Calcd for $NdCl_3 \cdot C_8H_{16}O_2$: Nd, 36.53; Cl, 26.98. Found: Nd, 36.50; Cl, 26.45.

Catalyst Preparation. Into a predried Schlenk tube containing several glass beads was introduced a weighed quantity of $NdCl_3 \cdot 2THF$ (e.g., 0.065 g, 1.65×10^{-4} mol). A calculated quantity of dried solvent (e.g., 6.1 mL) was added. Then the mixture was shaken for several minutes and a calculated quantity of $AlEt_3$ (e.g., 0.45 mL, 3.3×10^{-3} mol) was added with a syringe. The resulting suspension could be used for polymerization after aging it about 1 h. For the catalyst, the Al/Nd ratio was 20 (mole/mole) and the neodymium concentration was 2.5×10^{-2} M. Varying the relative amounts of catalyst precursor and $AlEt_3$ altered the catalyst activity and $[\eta]$ of the obtained polymers.

Polymerization Procedure. Polymerizations were carried out in 30-mL glass tubes under an Ar atmosphere, carefully excluding moisture and air. The reagents were introduced into this tube in the following order: first the monomer (or monomer solution), then the catalyst suspension, and finally the solvent. The polymerization reaction was carried out at a given temperature for a given time (see Discussion). The polymerization was terminated by adding an ethanol solution that contained antioxidant or by carboxylation. The resulting polymer was precipitated with an excess of ethanol and dried under vacuum below 50 °C to a constant weight. The conversion percent of polymerization was calculated based on the quantities of monomers used and polymer obtained. When carbon dioxide was used to terminate the polymerization reaction, the carbon dioxide was passed into the reactor after polymerization of butadiene was complete. The obtained product contained a carboxylate absorption by IR (1560 cm^{-1}). When this polymer was allowed to react further with *p*-toluenesulfonic acid or hydrochloric acid at about 70 °C, polymer containing carboxylic acid groups formed ($\nu_{C=O}$ 1725 cm^{-1}).

Polymer Characterization. Infrared spectra of polymer films on NaCl plates were recorded on an SP3-200 spectrophotometer. The relative amounts of *cis*-1,4-, 1,2-, and *trans*-1,4-polybutadiene were determined by measuring the corresponding optical density D_ν at ν = 738, 911, and 967 cm^{-1}, respectively. For polyisoprene the relative amount of 1,4 and 3,4 structure was determined by D_ν at ν = 840 and 890 cm^{-1}, respectively. ^{13}C NMR spectra of polyisoprene in dichloromethane solution were obtained with an FT-80 spectrometer. The intrinsic viscosity $[\eta]$ of these polymers was determined with an Ubbelohde viscosimeter in toluene solutions at 30 °C.

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